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Modelling butanol production in anaerobic mixed microbial cultures

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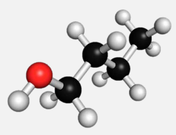
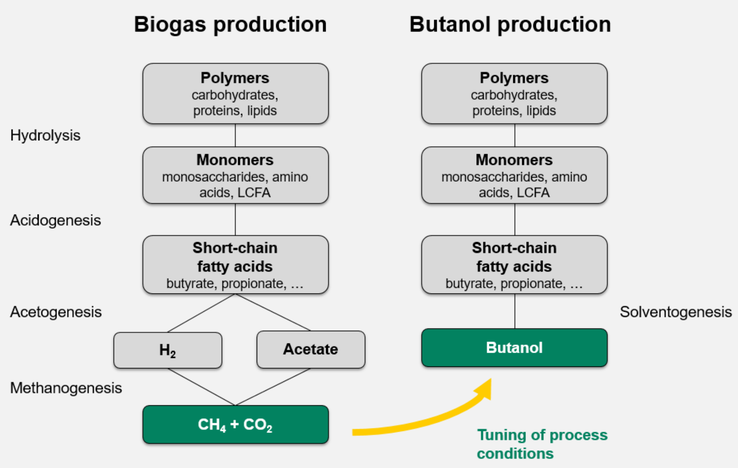
Introduction

Butyrate and hydrogen are common intermediates of anaerobic digestion and can be converted into butanol (Eq.1) using anaerobic mixed microbial cultures [1]. **Butanol is an energy-rich C4 alcohol** which is used in various industries, ranging from coatings to cosmetics. With an energy density 50% higher than ethanol, it is one of the most promising transport biofuels.

Eq.1 $2\ H_2 + Butyrate^- + H^+ \rightarrow Butanol + H_2O \quad \Delta G^{01} = -13.6$ kJ/mol



More recently, butanol production was observed in an anaerobic enrichment under bicarbonate limiting conditions [2]. These observations highlight the concept that certain operating conditions can trigger **butanol formation from waste streams**.



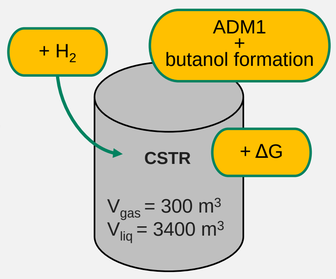
Objectives

- To predict optimum conditions for waste-based butanol production in a continuous full-scale anaerobic digester
- To study the impact of thermodynamics
- To determine an upper theoretical limit for butanol productivity

Methodology

The anaerobic digestion process is described using the ADM1 BSM2 implementation [3] of the Anaerobic digestion model No.1 (ADM1) [4]. The model is upgraded by implementing

- Butanol formation from butyrate and hydrogen (see Eq.1)
- Hydrogen supply to the reactor headspace
- Butanol gas-liquid mass transfer
- Thermodynamic limitation of acetogenesis, methanogenesis and butanol formation following [5] under consideration of a minimum energy quantum of 20 kJ/mol
- An improved description of the physicochemical processes (e.g. reactant activities instead of concentrations) according to [6].



Biomass yields on substrate are estimated according to the Gibbs energy dissipation method [7] and maximum biomass-specific conversion rates are calculated according to [8]. In all estimations, an average error of 15 % is assumed.

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Results

The energy gain from butanol formation cannot sustain microbial life under standard conditions. However, thermodynamic analysis reveals feasible conditions at low pH and increased hydrogen partial pressure (Fig. 1).

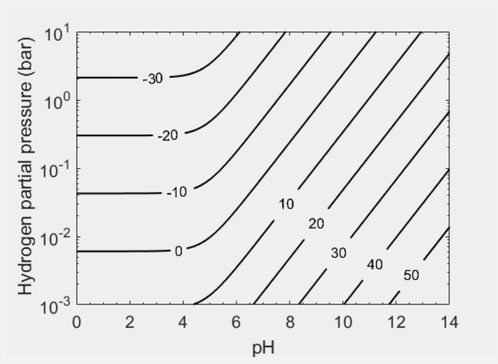

Figure 1: Gibbs energy change, ΔG1 (kJ/mol butanol), of butanol formation as a function of the hydrogen partial pressure and pH. A temperature of 35°C and a butyrate/butanol ratio equal to one are assumed.

Methane formation dominates the regime above pH 6 and reaches a maximum close to pH 7 (Fig. 2). Butanol productivity commences below pH 6 and reaches a maximum of 2.4 MWh-butanol.d^{-1} just below pH 5. This is where methanogenesis ceases due to pH inhibition. A pH of 5 was chosen for subsequent simulations.

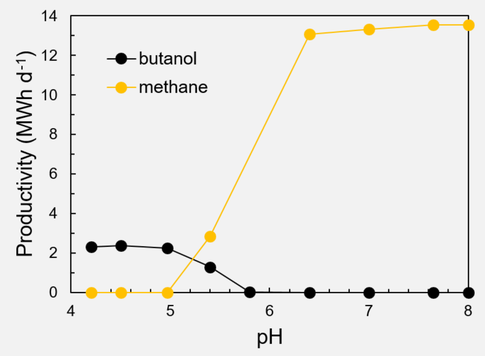

Figure 2: Butanol and methane production rates as a function of pH at 35 °C and P_{H2} = 0.9 bar. Results are obtained with the full model implementation.

A pronounced thermodynamic impact becomes apparent upon implementing thermodynamic limitations and additional hydrogen supply (Fig. 3). The default ADM1 implementation upgraded only by the butanol forming reaction overestimates butanol productivity by 120% as compared to the thermodynamics based implementation. External hydrogen supply results in a 66% increase in butanol productivity. A theoretical upper productivity limit is reached at 3.0 MWh-butanol.d^{-1}, where 99.9% of the butyrate available from acidogenesis are channeled towards butanol formation.

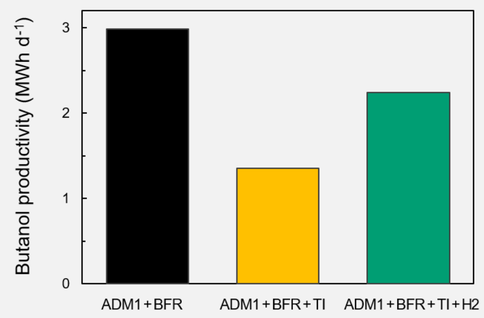

Figure 3: Butanol productivity at pH 5 and 35 °C. ADM1: the ADM1 model core, BFR: butanol-forming reaction, TI: thermodynamic inhibition function, H2: continuous H2 supply.

Elevated hydrogen partial pressures increase butanol productivity (Fig. 4). The lowest indicated partial pressure (0.47 bar) is reached without external hydrogen supply and results in the formation of 1.36 MWh-butanol.d^{-1}, corresponding to 6.1% of the biodegradable influent COD fraction. Butanol productivity is almost doubled (2.61 MWh-butanol.d^{-1}) at 1.4 bar, which results in 11.7% COD recovery.

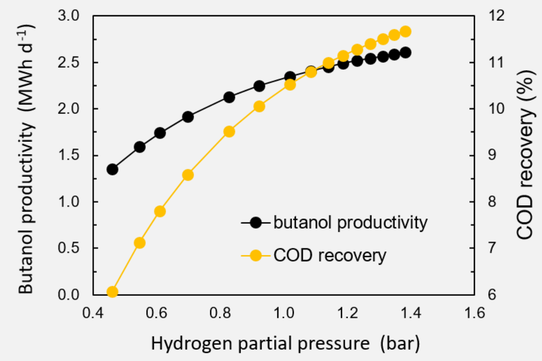

Figure 4: Butanol productivity and COD recovery as a function of the hydrogen partial pressure at pH 5 and 35 °C. Results are obtained using ADM1 with all extensions. COD recovery is calculated as butyrate consumed for butanol formation, divided by the biodegradable influent COD fraction.

Conclusions

- Butanol productivity is maximized at pH 5, where between 6% and 12% of the biodegradable influent COD are converted to butanol.
- Butanol productivity is overestimated by 120% when neglecting thermodynamic constraints.
- We propose a two-stage process for butanol/methane production in the frame of anaerobic digestion.